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Occupational exposure to PCDDs, PCDFs, and PCBs of metallurgical workers in some industrial plants of the Brescia area, northern Italy

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HIGHLIGHTS

- ▶ Dioxin/PCB haematic burdens of Brescia, Italy, metallurgical workers were investigated.
- ▶ Chemicals were measured in "professionally" (PE) and "not professionally" (NPE) exposed subjects.
- ▶ A significant difference was observed between PE data and a subgroup of NPE data (rural subjects).
- ▶ Increased haematic burdens of PE subjects were associated with certain workplace environments.

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ABSTRACT

Background: The study was carried out in order to respond to public concern on the occupational exposure of metallurgical workers to highly toxic PCDDs, PCDFs, and PCBs in the area of the city of Brescia, northern Italy.
Objectives: The study investigated the effects on the haematic burden of occupational exposures to the aforesaid contaminants in different work environments, attempting to establish causal relationships and providing indications for occupational health preventive measures.
Methods: Chemical concentrations were measured in blood serum of "professionally exposed" (PE) and "not professionally exposed" (NPE) subjects. NPE subjects included industrial administrative employees, Brescia inhabitants, and remote rural people.
Results: The central tendency indexes of contaminant cumulative concentrations were higher in PE than in NPE samples (for the mean values: PCDDs + PCDFs, 22.9 vs. 19.5 pgWHO-TEQ_{1997}/g lb; DL-PCBs, 26.0 vs. 23.6 pgWHO-TEQ_{1997}/g lb; PCDDs + PCDFs + DL-PCBs (TEQ_{TOT}), 48.9 vs. 43.1 pgWHO-TEQ_{1997}/g lb; Σ_6[NDL-PCBs], 427 vs. 401 ng g^{-1} lb); however, no statistical differences were detected at $P = 0.05$. A significant difference for PCDDs + PCDFs and TEQ_{TOT} was observed as the NPE data were progressively reduced to those of the remote rural people. The existence of a differential occupational exposure due to different environments was detected by applying the factor analysis to congener-specific data (analytical profiles).
Conclusions: Findings indicate that metallurgical workers may be exposed to PCDD, PCDF, and PCB more than the general population, in particular due to non-negligible contributions to exposure from workplace ambient air. Findings also suggest that an improvement of preventive measures may be required to avoid chemical overexposure in certain metallurgical workplaces. To identify exposure groups, the DL- and NDL-PCB analytical profiles seemed to be more sensitive to environmental exposure sources/pathways than those of PCDDs and PCDFs.

1. Introduction

Polychlorinated dibenzodioxins (PCDDs), dibenzofurans (PCDFs) and biphenyls (PCBs) are toxic, bioaccumulative, and persistent chemicals whose health effects include dermal toxicity, immunotoxicity, reproductive and endocrine disrupting effects, teratogenicity, and carcinogenicity (EC, 2001). As known, PCBs are

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industrial chemicals massively produced in many countries for over four decades (Fiedler, 2001; Holoubek, 2001; WHO, 2003). In fires and other thermal events, PCBs can be converted to PCDFs and other products (Erickson, 1989; De Felip et al., 1994). PCDDs and PCDFs—also collectively known as "dioxins"—are unintentional by-products released in a number of chemical processes as well as in other human activities, mainly including combustion processes (Bumb et al., 1980).

In the past three decades, the potential adverse effects of the aforesaid substances on human health prompted European Union (EU) regulatory authorities to define a wide range of measures to reduce their release into the environment and the food web. These measures have resulted in a substantial decrease of environmental and human levels of said compounds since the mid-1980s. However, PCDDs, PCDFs, and PCBs are still present in the environment, can be released from reservoir compartments (Fries, 1995; Holoubek, 2001; Fiedler, 2003; WHO, 2003), and continue to bioaccumulate in the food web (EC, 2001).

After the progressive abatement of emissions from non-hazardous waste incineration, once the largest source of PCDD and PCDF release into the atmosphere, other industrial processes—such as hazardous waste incineration and releases from the metallurgical industry—have likely become more important in the total inventory, providing relevant contributions of PCDDs, PCDFs, and possibly PCBs to their environmental burden (Li et al., 2010; Fang et al., 2011). The European Commission identified in iron ore sintering, electric-arc furnaces, and non-ferrous metal sintering important sources of PCDD and PCDF emissions to air (EC, 2001). In many countries, metallurgical processes were found to be the major contributors to the release of such compounds into the environment (Anderson and Fisher, 2002; Chen, 2004).

Relative to the general population, workers of the metallurgical industry can experience an increased exposure to PCDDs and PCDFs (Sweetman et al., 2004; Aries et al., 2008; Lee et al., 2009; Jackson et al., 2011). Though the diet accounts for more than 90% of the general population's total exposure to PCDDs, PCDFs, and PCBs, under specific circumstances contributions from environmental sources (including workplace) could play an important role in body burden building up (Bosch de Basea et al., 2011; Hsu et al., 2011). Indeed, the few occupational biomonitoring studies carried out on metallurgical workers revealed an overexposure to PCDDs and PCDFs (Chen et al., 2006a, 2006b; Lee et al., 2009).

The area of Brescia, a highly industrialized city in the Lombardy Region (northern Italy), is characterized by the presence of several metallurgical plants and by the highest number of secondary smelters in Italy. In the same area was the Caffaro Company, running the only Italian PCBs-producing plant, operative between 1930 and 1984. The prolonged and combined industrial activity has resulted in a widespread PCDD, PCDF, and PCB presence in the environment and local food produce, higher than current background (CTS, 2003; Turrio-Baldassarri et al., 2007) to such an extent that the area was declared "site of national interest for remediation" by the Italian authorities. In this exposure scenario, a possible overexposure deriving from work-related activities may be of high importance in assessing the health risks of exposed personnel.

The present study, supported by the local health agency—Azienda Sanitaria Locale (ASL) of the city of Brescia—was prompted by public concern on specific exposure situations in local metallurgical plants: indeed, in 1999 the Lombardy Region health authority had warned the regional health agencies about a relevant PCDD and PCDF presence detected in emission dusts from electrical iron smelters. The assessment of internal dose was carried out by measuring the serum concentrations of PCDDs, PCDFs, dioxin-like PCBs (DL-PCBs), and a selection of non-dioxin-like PCBs (NDL-PCBs). The aim of the study was to investigate in metallurgical workers the effects on the haematic burden of exposures to the aforesaid contaminants in different work environments, attempt to establish causal relationships between workplace activities and biomonitoring outcome, and provide indications for occupational health preventive measures.

Table 1
Participating subjects and panorama of the pooled samples showing the number of individual contributions (specimens) to each pooled sample. All recruited subjects were males.

Sample classification (exposure environment and work department)				Sample specimens (*N*) and mean age (years)		Sample classification (exposure environment and work department)				Sample specimens (*N*) and mean age (years)	
Subjects professionally exposed (PE)											
01	Steel 1	Steel production	Fusion	10	40.2	18	Steel 3	Steel production	Fusion	10	47.6
02	Steel 1	Steel production	Fusion	9	39.9	19	Steel 3	Steel production	Scrap handling	9	45.1
03	Steel 1	Steel production	Casting	10	43.2	20	Steel 3	Steel production	Casting	14	46.3
04	Steel 1	Steel production	Casting	10	42.8	21	Steel 3	Steel production	Maintenance	7	42.7
05	Steel 1	Steel production	Casting	10	44.0	22	Aluminum 1	Aluminum production	Fusion	9	46.3
06	Steel 1	Steel production	Scrap handling	12	47.7	23	Aluminum 1	Aluminum production	Casting	10	42.0
07	Steel 1	Steel production	Maintenance	8	42.0	24	Aluminum 1	Aluminum production	Scrap handling	6	46.8
08	Steel 1	Steel production	Maintenance	8	42.4	25	Aluminum 1	Aluminum production	Maintenance	8	48.3
09	Steel 2	Steel production	Casting	10	44.6	26	Aluminum 1	Aluminum production	Scrap handling	5	41.2
10	Steel 2	Steel production	Casting	10	43.3	27	Aluminum 1	Aluminum production	Maintenance	6	47.3
11	Steel 2	Steel production	Casting	10	43.0	28	Aluminum 2	Aluminum production	Mixed	10	44.6
12	Steel 2	Steel production	Fusion	10	41.3	29	Brass 1	Brass production	Fusion	9	44.8
13	Steel 2	Steel production	Fusion	10	36.2	30	Brass 1	Brass production	Fusion	9	44.6
14	Steel 2	Steel production	Maintenance	8	44.3	31	Brass 3	Brass production	Fusion	9	46.8
15	Steel 2	Steel production	Maintenance	7	36.6	32	Cast iron 1	Cast iron production	Fusion	7	42.9
16	Steel 2	Steel production	Scrap handling	6	46.3	33	Cast iron 2	Cast iron production	Mixed	10	41.0
17	Steel 2	Steel production	Scrap handling	6	44.3	34	Cast iron 3	Cast iron production	Mixed	8	46.3
Subjects not professionally exposed (NPE)											
01	Industrial environment (administrative employees)			10	37.9	07	Rural environment (remote subjects)			9	35.3
02	Industrial environment (administrative employees)			10	39.3	08	Rural environment (remote subjects)			10	33.5
03	Urban environment (Brescia inhabitants)			13	38.9	09	Rural environment (remote subjects)			9	39.7
04	Urban environment (Brescia inhabitants)			11	46.7	10	Rural environment (remote subjects)			9	39.9
05	Urban environment (Brescia inhabitants)			11	46.7	11	Rural environment (remote subjects)			10	39.0
06	Urban environment (Brescia inhabitants)			11	47.1						

2. Methods

2.1. Subject selection and recruitment

Study participants were recruited from the adult male population (age, 21–63 years) of the Lombardy Region under the coordination of the local health authority (Brescia ASL). In order to assess if the occupational exposure to the chemicals of interest could have an impact on their body burden, "professionally exposed" (PE) and "not professionally exposed" (NPE) subjects were selected for the study (Table 1). PE subjects ($N = 300$; participation rate = 77%) were recruited through occupational physicians from 10 metallurgical plants (ferrous and non-ferrous foundries), of which three produced steel, three cast iron, two aluminum, and two brass. Except where noted, NPE subjects ($N = 113$; participation rate = 69%) were recruited through the local network of general practitioners on the basis of three criteria: industrial NPE subjects ($N = 20$, recruited through occupational physicians) were administrative employees from one of the metallurgical plants also used to recruit PE workers; urban NPE subjects ($N = 46$) were people living in the city of Brescia; rural NPE subjects ($N = 47$) were people living in rural areas of the Brescia province. Additional details in Supplemental Material.

2.2. Serum collection and specimen pooling

Serum collection was carried out between January 2008 and December 2009 by the Brescia ASL personnel. About 50 mL of blood were withdrawn from each subject and centrifuged to obtain serum. A total of 413 individual serum specimens were collected from 300 PE and 113 NPE subjects and pooled to yield 34 PE and 11 NPE samples, respectively (Table 1). The (mean) age of pooled samples spanned 33.5–48.3 years. PE samples were obtained by aggregating serum specimens of subjects selected on the basis of work history similarities using as characterizing factors age, working age, exposure environment, work department, and company. For NPE samples, specimens were pooled primarily according to age and place of residence, excluding subject professionally exposed to metallurgical works. Additional details in Supplemental Material.

2.3. Analysis

PCDDs, PCDFs, and DL-PCBs in serum samples were analyzed by high resolution gas chromatography coupled with high resolution mass spectrometry (HRGC-HRMS), by an in-house adaptation of US EPA Method 1613; NDL-PCBs were assayed by HRGC coupled with low resolution MS (Ingelido et al., 2008; Miniero et al., 2011). Cumulative concentrations of PCDDs, PCDFs, and DL-PCBs were expressed as dioxin toxicity equivalents (TEQ) by using the 1997 WHO-TEF system (Van den Berg et al., 1998). Additional details in Supplemental Material.

2.4. Statistical analysis

The non-parametric Mann–Whitney U test and Kruskall–Wallis test (STATISTICA, Version 8.0) were used to investigate the statistical significance of the differences between groups in contaminants' serum concentrations. The available data were also analyzed by the general linear models (GLMs) and factor analysis (FA) procedures (STATGRAPHICS Centurion XVI).

GLMs were utilized to verify whether one or more factors (exposure environment, work department, worker's age) had a significant impact on one or more log-transformed dependent variables (PCDD + PCDF TEQ, DL-PCB TEQ, and Σ_6[NDL-PCB] analytical concentrations).

Table 2
Descriptive statistics[a] of the serum concentrations in samples of subjects professionally exposed (PE) and not professionally exposed (NPE). Values rounded off to three figures.

Contaminant[b]	N	X_{MIN}	X_{MED}	$\langle X \rangle$	SD	X_{MAX}
PE pooled samples						
PCDDs + PCDFs, pgWHO-TEQ$_{1997}$/g lb	34	13.6	22.2	22.9	6.5	45.7
DL-PCBs, pgWHO-TEQ$_{1997}$/g lb	31[c]	15.5	24.7	26.0	8.5	56.6
TEQ$_{TOT}$, pgWHO-TEQ$_{1997}$/g lb	31[c]	32.5	47.2	48.9	11.9	84.8
Σ_{30}[NDL-PCBs], ng g^{-1} lb	34	321	621	647	245	1460
Σ_6[NDL-PCBs], ng g^{-1} lb	34	227	403	427	171	1050
NPE[d] pooled samples						
PCDDs + PCDFs, pgWHO-TEQ$_{1997}$/g lb	11	14.5	19.1	19.5	5.1	29.6
DL-PCBs, pgWHO-TEQ$_{1997}$/g lb	11	18.6	22.9	23.6	3.2	28.5
TEQ$_{TOT}$, pgWHO-TEQ$_{1997}$/g lb	11	35.3	41.9	43.1	6.9	55.5
Σ_{30}[NDL-PCBs], ng g^{-1} lb	11	402	568	587	121	826
Σ_6[NDL-PCBs], ng g^{-1} lb	11	265	380	401	96	616
Urban + rural NPE pooled samples						
PCDDs + PCDFs, pgWHO-TEQ$_{1997}$/g lb	9	14.5	16.4	18.3	4.2	26.0
DL-PCBs, pgWHO-TEQ$_{1997}$/g lb	9	18.6	22.9	23.5	3.4	28.5
TEQ$_{TOT}$, pgWHO-TEQ$_{1997}$/g lb	9	35.3	38.0	41.8	6.2	51.2
Σ_{30}[NDL-PCBs], ng g^{-1} lb	9	402	586	609	122	826
Σ_6[NDL-PCBs], ng g^{-1} lb	9	265	395	419	97	616
Rural NPE pooled samples						
PCDDs + PCDFs, pgWHO-TEQ$_{1997}$/g lb	5	14.5	14.7	15.2	0.8	16.4
DL-PCBs, pgWHO-TEQ$_{1997}$/g lb	5	20.6	21.7	22.9	2.9	27.9
TEQ$_{TOT}$, pgWHO-TEQ$_{1997}$/g lb	5	35.3	37.7	38.0	3.2	43.4
Σ_{30}[NDL-PCBs], ng g^{-1} lb	5	553	586	623	75	709
Σ_6[NDL-PCBs], ng g^{-1} lb	5	363	380	409	50	471

[a] N, number of items; X_{MIN}, minimum value; X_{MED}, median; $\langle X \rangle$, arithmetic mean; SD, standard deviation; X_{MAX}, maximum value.
[b] Σ_{30}[NDL-PCBs]: sum of the concentrations of PCBs 18, 28, 31, 33, 49, 52, 66, 70, 74, 91, 95, 99, 101, 110, 128, 138, 141, 146, 149, 151, 153, 170, 174, 177, 180, 183, 187, 194, 196, and 203. Σ_6[NDL-PCBs]: sum of the concentrations of PCBs 28, 52, 101, 138, 153, and 180.
[c] DL-PCBs 77, 81, 126, and 169 were not determined in three PE samples. The pertinent TEQ values were absent in the statistical evaluations.
[d] Industrial (not professionally exposed), urban, and rural subjects.

FA was adopted to explore biomonitoring data variability (Jolliffe, 1986; Fielding, 2007). Before performing FA, data were log-transformed to reduce the effect of data dispersion; congeners with a non-detect frequency across the database greater than 40% were excluded from the analysis. FA is designed to extract common factors (typization/characterization) from a set of quantitative variables (congeners) in a fashion similar to the principal component analysis (PCA); however, FA is concerned solely with correlations between variables. Indeed, FA assumes that observed correlations are caused by some underlying patterns in the data (Fielding, 2007). The "varimax" method, used to rotate the factor loading matrix, maximizes the variance of the loadings in each factor group. Only the (positive) loadings with values greater than 50% of each factor's maximum value were selected to describe the data set (Jolliffe, 1986). The most important FA loadings describing the data sets do not necessarily correspond to the most abundant variables dealt with.

3. Results and discussion

3.1. Description of biomonitoring results

The results obtained for the two groups of PE and NPE subject pooled samples are statistically described and compared in Tables 2 and 3, respectively.

Table 3
Results of the application of Mann–Whitney U test to serum concentrations in pooled samples of subjects professionally exposed (PE) and not professionally exposed (NPE).

Contaminant [a]	*N*	*N*	Rank sum		U	*P*
Samples PE vs. samples NPE	PE	NPE	PE	NPE		
PCDDs + PCDFs, pgWHO-TEQ_{1997}/g lb	34	11	845	190	124	0.10
DL-PCBs, pgWHO-TEQ_{1997}/g lb	31[b]	11	687	216	150	0.56
TEQ_{TOT}, pgWHO-TEQ_{1997}/g lb	31[b]	11	710	193	127	0.21
Σ_{30}[NDL-PCBs], ng g^{-1} lb	34	11	800	235	181	0.63
Σ_6[NDL-PCBs], ng g^{-1} lb	34	11	788	247	169	0.87
Samples PE vs. samples urban + rural NPE[c]	PE	Urban + rural NPE	PE	Urban + rural NPE		
PCDDs + PCDFs, pgWHO-TEQ_{1997}/g lb	34	9	822	124	79	0.03
DL-PCBs, pgWHO-TEQ_{1997}/g lb	31[b]	9	654	166	121	0.55
TEQ_{TOT}, pgWHO-TEQ_{1997}/g lb	31[b]	9	681	139	94	0.14
Σ_{30}[NDL-PCBs], ng g^{-1} lb	34	9	749	197	143	0.98
Σ_6[NDL-PCBs], ng g^{-1} lb	34	9	738	208	152	0.77
Samples PE vs. samples rural NPE[d]	PE	Rural NPE	PE	Rural NPE		
PCDDs + PCDFs, pgWHO-TEQ_{1997}/g lb	34	5	756	24	9	0.001
DL-PCBs, pgWHO-TEQ_{1997}/g lb	31[b]	5	590	76	61	0.45
TEQ_{TOT}, pgWHO-TEQ_{1997}/g lb	31[b]	5	617	49	34	0.05
Σ_{30}[NDL-PCBs], ng g^{-1} lb	34	5	676	104	81	0.87
Σ_6[NDL-PCBs], ng g^{-1} lb	34	5	675	105	80	0.83

[a] Σ_{30}[NDL-PCBs]: sum of the concentrations of PCBs 18, 28, 31, 33, 49, 52, 66, 70, 74, 91, 95, 99, 101, 110, 128, 138, 141, 146, 149, 151, 153, 170, 174, 177, 180, 183, 187, 194, 196, and 203. Σ_6[NDL-PCBs]: sum of the concentrations of PCBs 28, 52, 101, 138, 153, and 180.
[b] DL-PCBs 77, 81, 126, and 169 were not determined in three PE samples.
[c] Industrial NPE data removed from statistical analysis.
[d] Industrial and urban NPE data removed from statistical analysis.

Cumulative concentrations in PE and NPE samples (Table 2) of PCDDs + PCDFs, DL-PCBs, and PCDDs + PCDFs + DL-PCBs (TEQ_{TOT}) fall respectively in the ranges 13.6–45.7 and 14.5–29.6, 15.5–56.6 and 18.6–28.5, and 32.5–84.8 and 35.3–55.5 pgWHO-TEQ/g lb (lipid base); in the same groups, NDL-PCB concentrations (Σ_{30}[NDL-PCB]) are respectively comprised in the ranges 321–1460 (Σ_6[NDL-PCB], 227–1050) ng g^{-1} lb and 402–826 (Σ_6[NDL-PCB], 265–616) ng g^{-1} lb. The central tendency indexes (medians and arithmetic means) of all the considered contaminants are higher in PE samples, yet all NPE sample data are comprised within the range of values covered by the PE samples. Table 2 also summarizes the cumulative concentrations of the aforesaid chemicals in the urban + rural and rural NPE subgroups.

The application of the Mann–Whitney U test did not show any statistically significant ($P > 0.05$) difference between PE and NPE data (Table 3); only a marginal significance ($P = 0.1$) was found for PCDDs + PCDFs. When the test was applied after removing from the NPE data the results relative to the two industrial NPE samples (industry administrative employees), the difference of PCDD + PCDF concentrations in PE and NPE samples became significant ($P = 0.03$). This outcome suggests that the subjects employed in administrative roles in the metallurgical company where they were recruited may have experienced an incremental exposure from the diffuse indoor presence of the contaminants dealt with. When the contribution of subjects living in the area of Brescia (urban NPE, four samples) was removed from NPE data, the difference of PCDD + PCDF concentrations between PE and NPE data (rural environment only) grew to be more significant ($P = 0.001$): for instance, the ratio of means $[\langle X \rangle_{PE}] \times [\langle X \rangle_{NPE}]^{-1}$ was 1.17, 1.25, and 1.51, respectively when the entire distributions were compared, after removal of industrial NPE subjects from the NPE data set, and when only rural subjects were left in the NPE data set. Concurrently, TEQ_{TOT} values also reached a significant ($P = 0.05$) difference when only rural subjects were present in the NPE data set. For the other contaminants, no relevant changes in significance were observed when applying the Mann–Whitney U test after the stepwise exclusion of NPE sample data.

The results described may be explained by considering the widespread and marked presence of PCDDs, PCDFs, and PCBs in the area of Brescia, where the environmental concentrations of

Table 4
Factor loadings from the factor analysis of congener analytical concentrations. The most important variables are in bold. Σ indicates a sum of congener analytical concentrations.

Congeners	Factors				
	1	2	3	4	5
2,3,7,8-T_4CDD	−0.098	**0.644**	−0.409	0.202	−0.046
1,2,3,7,8-P_5CDD	0.190	0.085	−0.055	0.047	**0.946**
1,2,3,4,7,8-H_6CDD	**0.758**	0.144	0.242	0.094	0.263
1,2,3,6,7,8-H_6CDD	**0.595**	**0.526**	0.123	−0.376	−0.247
1,2,3,7,8,9-H_6CDD	**0.772**	0.001	−0.141	0.223	0.282
1,2,3,4,6,7,8-H_7CDD	0.034	0.220	−0.038	**0.848**	0.203
O_8CDD	−0.666	−0.403	−0.242	−0.317	0.199
2,3,4,7,8-P_5CDF	0.343	**0.816**	0.398	−0.008	0.001
1,2,3,4,7,8-H_6CDF	**0.398**	0.306	**0.759**	0.217	0.005
1,2,3,6,7,8-H_6CDF	0.334	0.310	**0.830**	0.150	0.018
2,3,4,6,7,8-H_6CDF	0.355	−0.124	0.155	0.719	−0.167
1,2,3,4,6,7,8-H_7CDF	−0.197	−0.100	**0.738**	−0.098	−0.091
Σ_{12}[PCDDs + PCDFs]	−0.156	−0.805	−0.199	−0.035	−0.237

	1	**2**	**3**
PCB 105	**0.850**	−0.225	0.135
PCB 114	−0.401	−0.458	−0.634
PCB 118	**0.892**	−0.225	−0.283
PCB 126	**0.502**	**0.631**	−0.256
PCB 156	−0.925	0.090	−0.221
PCB 157	−0.196	0.238	**0.809**
PCB 167	−0.090	**0.759**	0.085
PCB 169	−0.364	**0.716**	0.009
PCB 189	0.129	−0.290	**0.713**
Σ_9[DL-PCBs]	−0.146	**0.474**	0.058

	1	**2**	**3**	**4**
PCB 28	**0.784**	−0.012	−0.302	−0.113
PCB 52	**0.840**	−0.100	−0.431	−0.188
PCB 95	**0.830**	0.399	0.103	0.211
PCB 99	0.168	**0.869**	−0.140	−0.075
PCB 101	**0.861**	0.246	0.036	0.211
PCB 110	**0.772**	0.286	0.078	0.070
PCB 128	0.324	**0.752**	−0.031	0.093
PCB 138	−0.224	**0.824**	−0.254	0.151
PCB 146	−0.218	0.372	0.024	**0.698**
PCB 153	−0.583	0.067	−0.060	**0.475**
PCB 170	0.127	−0.191	**0.803**	0.001
PCB 177	0.084	0.034	−0.124	**0.810**
PCB 180	−0.122	−0.288	**0.844**	−0.088
PCB 183	−0.821	0.085	−0.171	0.056
PCB 187	**0.500**	−0.241	0.138	**0.591**
Σ_{15}[NDL-PCBs]	−0.090	−0.659	0.397	−0.114

Table 5
Factor scores from factor analysis of congener analytical concentrations. Rounding off to one decimal figure.

Sample ID	Factors											
	PCDDs and PCDFs					DL-PCBs			NDL-PCBs			
	1	2	3	4	5	1	2	3	1	2	3	4
PE 01	−0.7	−0.9	0.0	0.0	0.6	1.4	−1.9	1.0	**12.0**	3.0	0.8	−1.2
PE 02	−3.4	−0.4	−0.7	−2.4	0.8	3.4	0.5	−0.8	**3.0**	2.5	−0.1	0.1
PE 03	0.3	0.7	0.7	0.3	0.6	**0.8**	−2.6	−0.7	**1.1**	−0.9	1.6	−0.7
PE 04	0.2	0.0	0.1	−0.1	0.9	**2.7**	−2.0	−0.9	**1.0**	1.0	0.8	−2.8
PE 05	−0.6	0.7	1.9	0.6	−0.3	**1.9**	−2.5	−1.0	**2.1**	−1.3	1.9	−3.6
PE 06	−2.1	2.3	2.0	−2.5	0.6	1.3	−0.2	−0.7	**1.2**	0.9	0.8	0.0
PE 07	−1.4	−1.2	−0.5	−0.4	0.3	−1.3	1.4	−0.5	**1.3**	1.3	1.1	−1.2
PE 08	−1.7	−0.9	1.1	−0.4	0.1	3.1	1.0	−1.7	**2.3**	0.5	1.0	−0.4
PE 09	−2.9	−0.9	−0.5	−1.3	−2.9	**2.3**	1.3	1.8	**2.9**	1.9	−0.1	−0.9
PE 10	−1.1	1.6	1.5	0.2	−1.8	**1.7**	4.0	3.3	**0.7**	0.3	−0.1	−0.7
PE 11	1.3	0.2	−0.1	0.0	1.4	**2.2**	0.5	2.5	**4.6**	4.5	−2.1	1.7
PE 12	7.1	5.8	7.2	−3.6	−1.8	−0.4	0.0	0.2	−4.3	−1.9	−0.2	−1.4
PE 13	−4.0	−5.2	−4.0	−2.4	−1.8	4.7	2.4	3.0	**5.6**	4.7	−1.8	0.0
PE 14	7.1	3.8	7.5	1.9	−3.1	2.8	1.5	0.0	**1.1**	0.9	−0.4	2.7
PE 15	−0.4	1.8	1.2	−0.1	−1.2	0.1	2.5	3.8	0.2	1.2	−0.2	0.8
PE 16	−1.5	0.7	−0.8	−0.6	−1.8	1.9	1.0	0.3	**2.2**	1.7	−1.6	0.3
PE 17	3.1	1.7	−1.0	−0.4	2.4	−0.9	3.4	3.7	**4.4**	1.9	0.1	−0.2
PE 18	−1.2	−1.0	0.2	−0.5	0.0	−0.9	−0.4	1.4	**2.8**	−4.4	3.4	2.1
PE 19	1.6	0.9	1.2	0.3	0.8	1.4	−1.8	0.8	**4.1**	1.0	0.8	2.6
PE 20	−2.2	−2.2	−1.0	−0.5	−0.5	0.0	−2.3	0.3	−0.5	−5.3	2.1	−0.4
PE 21	−3.8	−5.4	−3.0	−2.0	−0.3	−0.3	−3.1	0.6	0.2	0.2	−0.5	−0.8
PE 22	−2.9	−2.7	−4.8	−1.5	−0.7	0.9	−1.9	−0.4	**3.8**	0.4	**1.5**	−0.1
PE 23	2.4	3.8	−0.1	−1.8	0.2	2.8	−5.5	−2.1	**4.3**	5.9	−2.4	−0.7
PE 24	−2.0	−2.3	−1.6	−0.5	−0.6	−8.0	2.4	0.9	−1.0	−10.7	**5.5**	−1.2
PE 25	−0.6	−1.8	−5.2	−1.8	−0.6	−3.0	−0.1	0.7	**2.2**	−3.5	**2.8**	−0.3
PE 26	−2.8	−1.7	−2.4	0.4	−0.8	5.2	−4.9	0.1	**6.9**	7.3	−7.3	3.5
PE 27	−3.4	−1.9	−3.0	0.1	−1.3	−6.1	2.1	1.0	−3.1	−5.9	**3.7**	−2.2
PE 28	1.5	2.6	2.2	1.1	0.4	−4.1	−1.3	−0.2	0.2	−0.9	**0.9**	1.1
PE 29	−1.1	−3.4	−0.7	0.4	0.0	−0.9	**1.7**	−1.8	−6.6	−0.5	−0.3	0.3
PE 30	−1.1	−3.3	0.4	−0.1	−0.7	−4.9	**2.0**	−0.6	−7.5	−0.4	−0.2	−0.2
PE 31	−0.7	−4.9	3.2	2.0	−1.3	−2.2	**2.7**	−2.3	−5.0	0.0	−2.1	−1.2
PE 32	**5.3**	**4.9**	**3.4**	**3.2**	**1.8**	−2.3	0.3	0.3	**6.0**	−6.8	−4.3	−7.8
PE 33	**2.2**	**2.5**	**1.2**	**1.0**	**1.8**	−2.3	−1.5	−0.2	**0.4**	−1.3	0.8	1.4
PE 34	**5.4**	**5.6**	**5.1**	**3.0**	**1.6**	1.4	−0.6	−2.1	**2.7**	0.8	−2.4	3.5
NPE 01	**8.2**	**3.3**	2.7	**5.5**	3.5	**1.4**	**1.9**	−0.4	−3.2	0.7	−0.7	1.2
NPE 02	**6.2**	**4.5**	−0.4	**5.0**	2.1	**1.3**	**2.3**	0.9	1.1	2.2	−1.3	1.8
NPE 03	**1.6**	**4.9**	−0.6	**3.4**	−1.8	**3.7**	**0.6**	1.1	−2.5	0.2	−1.5	0.0
NPE 04	−2.7	−2.2	−2.3	−1.2	0.4	−8.0	**2.6**	−0.5	−12.5	−5.8	3.4	−2.0
NPE 05	−3.8	−3.7	−4.4	−0.7	−0.2	−0.2	**2.1**	−6.6	−12.6	2.3	−2.7	−1.1
NPE 06	−0.1	−0.7	−1.9	−0.5	0.5	−4.2	**2.0**	−2.6	−12.5	−1.4	0.9	−1.1
NPE 07	−1.2	−2.2	0.7	0.1	0.4	1.2	−2.5	−0.2	−1.0	1.5	−0.4	**0.8**
NPE 08	−0.4	1.0	0.1	−0.1	0.5	2.0	−2.7	−1.2	−2.2	2.0	−0.3	**2.6**
NPE 09	−3.1	−2.8	−2.2	−1.6	−0.1	−2.2	−0.4	0.7	−2.1	−2.1	1.7	**0.9**
NPE 10	−1.1	−1.0	−1.6	−1.0	0.8	−0.9	−2.0	−0.5	−2.6	1.1	−0.8	**2.6**
NPE 11	0.2	−0.8	−0.7	−0.2	0.9	1.5	−2.2	−0.1	−1.1	1.7	−1.7	**2.1**

the aforesaid contaminants are on the whole higher than in background areas elsewhere (CTS, 2003; Turrio-Baldassarri et al., 2007). The biomonitored PCDD + PCDF, DL-PCB, TEQ_{TOT}, and NDL-PCB concentrations also exhibit higher values than on average recorded in biomonitoring studies in other parts of Italy (Abballe et al., 2008; ASL Roma E, 2008; De Felip et al., 2004, 2008; Porpora et al., 2006, 2009). TEQ_{TOT} concentrations in samples from Veneto, Latium, and Tuscany Regions appear to range from 18 to 34 pgWHO-TEQ/g lb and occur on the lower side of the range reported for samples of this study and other biomonitoring studies carried out in the Brescia area (Donato et al., 2006; Turrio-Baldassarri et al., 2008; Bergonzi et al., 2009). NDL-PCB concentrations fall between 179 and 573 ng g^{-1} lb in samples from Latium, Marche, and Tuscany Regions, reach up to 2462 ng g^{-1} lb in samples from the area of Pavia (another city of the Lombardy Region) (Turci et al., 2006), and range between 83 and 38,679 ng g^{-1} lb in samples from the area of Brescia (Donato et al., 2006). Our findings provide a confirmation of the previous findings that show the people from the area of Brescia to be characterized by levels of haematic contamination tendentially higher than the Italian background. For details, see Table S1 in Supplemental Material.

TEQ_{TOT} concentrations in rural NPE samples show a tendency to be higher than those reported in other studies of the Italian general population (see above references). In the same NPE samples the cumulative NDL-PCB concentrations are comprised within those measured in the urban NPE samples and, with the exception of Pavia data, are in general higher than the NDL-PCB concentrations detected in people from other parts of Italy. These findings seem to indicate the presence of a diffuse PCB contamination in a large environment around Brescia, also including food-producing areas.

The PE sample data were analyzed in order to reveal possible differences in contaminant serum concentrations between workers employed in distinct productions (steel, aluminum, brass, and cast iron) and in distinct departments (fusion, casting, scrap handling, maintenance, and mixed). As to the first issue, the application of the Kruskall–Wallis test did not show statistically significant ($P > 0.05$) differences of the internal doses; however, the available data may be regarded as not suitable for a sound statistical evaluation due to the unbalance between data sets. Statistically significant differences were found in PCDD + PCDF ($P = 0.04$) and TEQ_{TOT} ($P = 0.007$) concentrations when the Kruskall-Wallis test was applied to the data of PE subjects working in diverse metallurgical

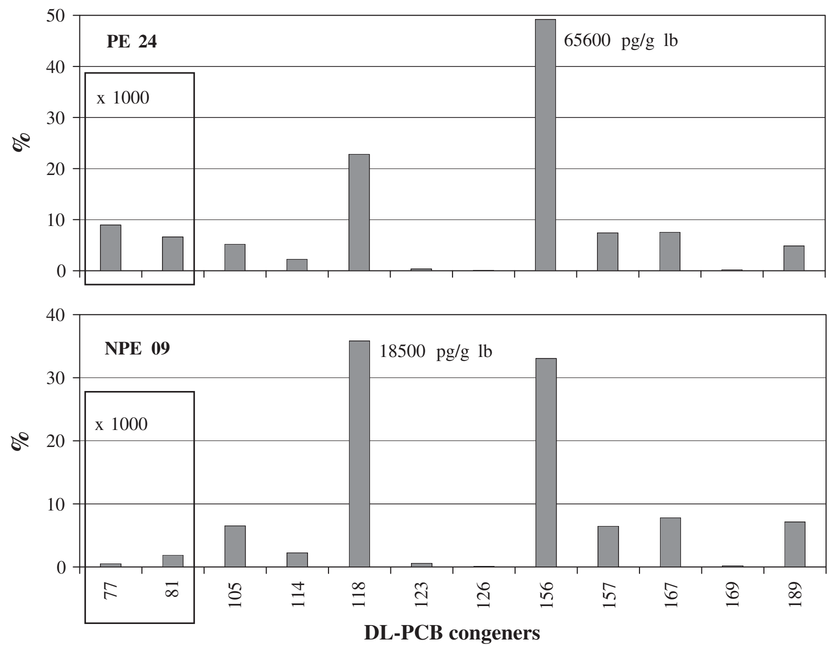

Fig. 1. Analytical profiles of DL-PCBs for typical exposure environments—scrap handling workers (PE 24) and remote (rural) subjects (NPE 09)—selected as they respectively represent the high and low levels of exposure within their own groups. Profiles are normalized against the sums set equal to 100 of the pertinent analytical congener concentrations.

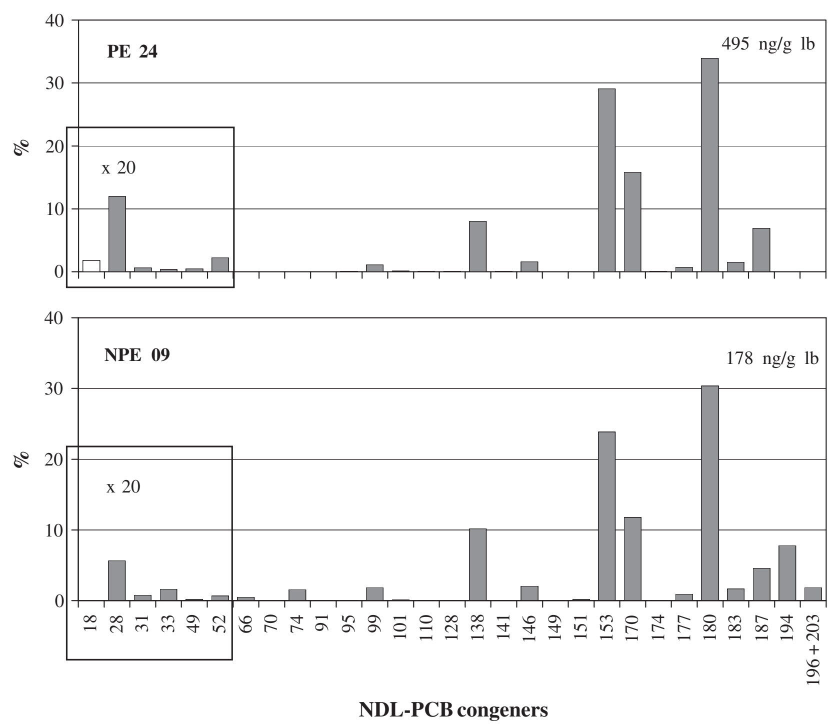

Fig. 2. Analytical profiles of NDL-PCBs for typical exposure environments—scrap handling workers (PE 24) and remote (rural) subjects (NPE 09)—selected as they respectively represent the high and low levels of exposure within their own groups. Profiles are normalized against the sums set equal to 100 of the pertinent analytical congener concentrations. The empty bar indicates a non-detect.

departments: in particular, the fusion and maintenance workers had higher levels of contamination relative to the other workers. The highest PCDD + PCDF concentrations were detected in the samples of melting shop workers, followed by the plant maintainers. PCDDs, PCDFs, and PCBs are likely to be released from the furnace owing to the presence of chloro-organic chemicals in the metal scrap (Figueira and Gomes, 2004; Sweetman et al., 2004; Aries et al., 2008). These compounds may participate in chemical reactions when scrap is charged into the furnace: during charging, the roof is removed and significant releases of fumes and particulate matter take place inside the melting shop, which may significantly affect indoor air quality and consequently inhalation exposure (Chen et al., 2006b; Aries et al., 2008). As to maintainers, they work in almost all the areas of a plant and exposure can take place through different pathways. It may be pointed out that the same worker can be assigned to different departments during his work history, and that the biomonitored internal doses are the result of all his working experiences.

The GLMs analysis applied to the measured internal doses yielded no statistical evidence of correlations for worker's age ($P \gg 0.05$) and NDL-PCB analytical concentrations ($P > 0.05$). In agreement with the non-parametric test results described above, PCDD + PCDF TEQ concentrations appeared to correlate significantly ($P \ll 0.05$) with exposure environments and work departments regardless of worker's age being entered as a confounder or not, whereas DL-PCB TEQ concentrations appeared to correlate ($P = 0.04$) only when the model took into account age as a confounding factor.

3.2. Factor analysis

According to the FA outcome, the PCDD + PCDF, DL-PCB, and NDL-PCB data sets were respectively described by five, three, and four factors (Table 4), with corresponding explained cumulative variances of 79.6%, 69.6%, and 74.0%. In the table, the most important loadings—i.e. those greater than 50% of each factor's maximum value—are shown in bold on gray background; the first column identifies only those congeners whose non-detect frequency across the database was not greater than 40%. On average, the exposure chemicals appear to be common among PE subjects and, in some cases, among the latter and NPE subjects. However, a number of specific features can be highlighted: the following evaluations were based on the availability of factor scores (Table 5), the final FA outcome. For exposure groups, refer to Table 1.

The analysis of NPE subjects driven by PCDDs + PCDFs allowed to classify NPE subjects 01–03. These samples—two from administrative employees and one from Brescia inhabitants—are typified by the scores of Factors 1, 2, and 4, NPE 01 and 02 exhibiting very high values in Factor 1. Among the different workplace exposure environments of PE subjects, the cast iron production (PE 32, 33, 34) was qualified by all the factors shown in Table 5, whereas aluminum, brass, and steel productions were not univocally nor principally typified by any factors.

As to DL-PCBs, the remote (rural NPE) subjects were not typified by any specific factor, whereas the two remaining NPE groups were typified by Factors 1 and 2 (Table 5) and variables DL-PCBs 105, 118, 126, 167, 169, and Σ_9[DL-PCBs] (Table 4). As to the administrative employees, the characterization overlapped the one observed for PCDDs + PCDFs; however, Brescia inhabitants (NPE 03–06) were better qualified by DL-PCB Factor 2. Among the different PE subjects, brass production was typified by Factor 2 (Table 5) and variables DL-PCBs 126, 167, 169, and Σ_9[DL-PCBs] (Table 4). Of the work environments, the casting groups had the best characterization, principally described by Factor 1 (PE 03–05, PE 09–11).

With reference to NDL-PCBs, the remote rural subjects (NPE 07–11) were typified by Factor 4: of the major congeners, NDL-PCB 153 was the variable that almost univocally characterized the rural NPE group, its loadings being substantially inconspicuous in Factors 1–3 (Table 4). The remaining NPE subjects were not univocally nor principally typified by any factors (Table 5). Among the PE subjects, the aluminum and steel production environments were those more typified, respectively by Factors 1 and 3 and by Factor 1. Similarly to DL-PCBs, in general the casting groups' environments had the best characterization, described by Factor 1. It can be observed that the highest score was associated with the steel fusion environment. Therefore, work type, production type, and company size appear to yield concurring results.

Figs. 1 and 2 provide examples of DL-PCB and NDL-PCB analytical profiles for typical exposure environments—scrap handling workers (PE 24) and remote (rural) subjects (NPE 09)—selected as they respectively represent high and low levels of exposure within their own groups. Profiles are normalized against the sums (set equal to 100) of congener analytical concentrations, so that the height of each bar (or congener) in a given profile is also the percent contribution of that congener to the sum. From the figures, it can be observed how the more volatile (but minor) components (DL-PCBs 77 and 81; NDL-PCBs 28 and 52) exhibit visible variations, with a remarkable increase in PE 24 relative to NPE 09. It is this variability, among other features, that seems to be captured by FA while looking for common factors of grouping. A feature worthwhile noticing is the remarkable concentration of DL-PCB 156 in both samples and in particular in sample PE 24, where it is responsible for almost 50% of DL-PCB cumulative concentration (in analytical units). More in general, as can be seen by comparing the results of this study to recent biomonitoring works carried out in Italy (Porpora et al., 2009; De Felip and di Domenico, 2010), DL-PCB 156 appears to be particularly prominent in subject groups of the Brescia area and, particularly, in the PE ones. In the light of the above, DL-PCB 156 might qualify as a specific biomarker for Brescia subjects.

4. Conclusions

The results of our biomonitoring study, carried out in northern Italy industries, indicate that metallurgical workers may be exposed to PCDD, PCDF, and PCB levels higher than those experienced by the general population, in particular due to non-negligible contributions to exposure from workplace ambient air. Higher internal doses in blood serum were found to be associated primarily with the fusion and casting processes and plant maintenance, presumably due to intake by inhalation as indicated by the FA procedure applied to chemical analytical profiles. On the whole, these findings suggest that an improvement of preventive measures may be required to avoid overexposure to some contaminants of metallurgical workers in certain workplaces.

The results relative to the serum concentrations of subjects living in the city of Brescia and its surroundings likely reflect the local PCDD, PCDF, and PCB contamination conditions deriving from the intense industrial activity that is typical of the area, having an impact also on rural districts quite distant from contamination sources.

The DL- and NDL-PCB analytical profiles detected in serum seemed to be more sensitive to environmental exposure sources/pathways than those of PCDDs and PCDFs. Exposure groups and production types were specifically identified (typified) by the FA procedure. In particular, the rural NPE groups (remote subjects) and the other NPE groups could be differentiated on the basis of internal dose factors, the former being distinguished specifically by NDL-PCB 153—a common human biomarker—while the latter by DL-PCBs only. PE subjects, in particular those exposed to casting, were univocally characterized by the low chlorinated NDL-PCBs 28 and 52, both quite volatile and therefore with a high potential to be accumulated *via* inhalation and reflecting a localized situation. Based on PCDD, PCDF, and PCB profiles detected by blood (serum) biomonitoring, different work environments could potentially be singled out; however, in our study steel production companies had a better characterization likely due to the greater number of observations.

Conflict of interest statement

The authors declare they have no competing financial interests.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.chemosphere.2012.06.073.

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